Femtosecond XUV-IR induced photodynamics in the methyl iodide cation

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ABSTRACT

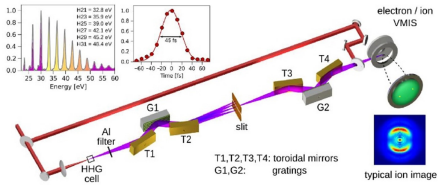
In this work, the role of a time-delayed moderately strong IR probe pulse on the XUV time-resolved dissociation dynamics of the methyl iodide cation (CH_3I^+) is investigated. In particular, CH_3I^+ is prepared in the ground $\tilde{X}\,^2E_{3/2,\,1/2}$ and excited $\tilde{A}\,^2A_1$ states using the 9th harmonic of 800 nm (13.95 eV) leading to CH_3^+ and I^+ fragments through different dissociation pathways. Velocity map imaging is employed to detect selected fragment ions – CH_3^+ and I+ – as well as photoelectrons. The experimental results are supported by high-level *ab initio* calculations of the potential energy curves, in combination with full dimension on-the-fly trajectory calculations on the $\tilde{A}\,^2A_1$ state in the absence and presence of the IR pulse. The results provide a detailed picture of the CH_3I^+ cation dissociation and the action mechanisms of the probe IR pulse.

METHODOLOGY

The output of a Ti:sapphire laser (1 kHz, 25 fs, 5 mJ, 800 nm) is split into two arms:

(I) Pump pulse: time delay compensating monochromator selects the 9th harmonic of 800 nm preserving the temporal duration (20-25 fs, 300 meV broad spectrum)

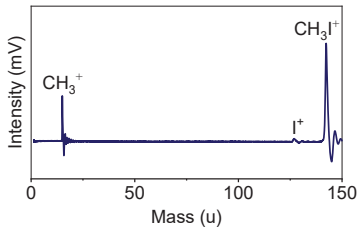
(II) Probe pulse: 800 nm pulses (25-35 fs, $1.3\cdot10^{13}$ W/cm^2 avoiding DPI or CEI).



Cross correlation: Ar sidebands 11th H + 800 nm: 36 ± 5 fs (+IR intensity at the focus).

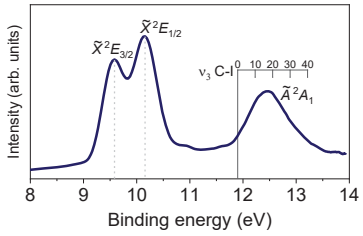
EXPERIMENTAL RESULTS

XUV ONLY – TOF MASS SPECTRUM



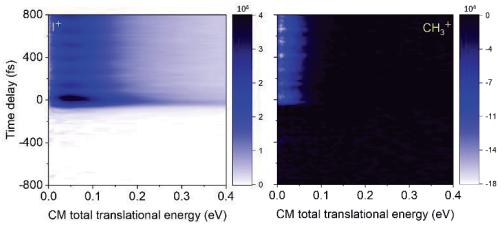
Increased CH_3^+ signal. The $\tilde{A}\,^2A_1$ state dissociates via internal conversion to the hot vibrational bands of the ground state leading to I + CH_3^+.

XUV ONLY - PHOTOELECTRON SPECTRUM



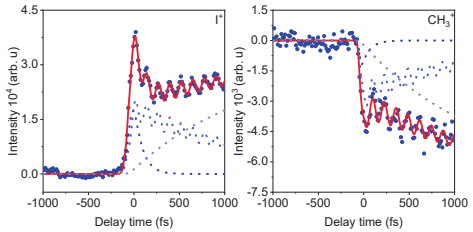
The cation is prepared in the $\tilde{X}\,^2E_{3/2,\,1/2}$ states and in the $\tilde{A}\,^2A_1$ state with high vibrational content (v=15).

KINETIC ENERGY RELEASE MAPS



Time-dependant low KER oscillatory structure at positive pump-probe delays. CH_3^+ yield decreases while I^+ yield increases with pump-probe delay.

TRANSIENTS

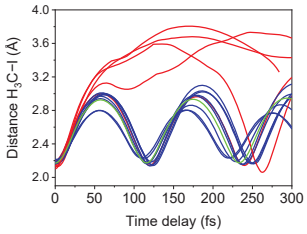


Transients reveal different components: an oscillatory structure, a slow component (1.3 ps) and a fast component (83 fs).

FFT analysis > oscillation period of 130 fs ~ C–I stretching mode (ν_3) in the excited $\tilde{A}\,^2A_1$ state of CH_3I^+.

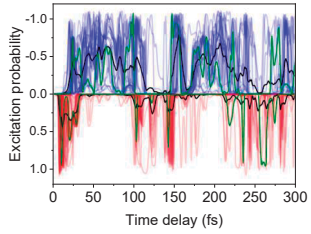
THEORETICAL CALCULATIONS (XMS-CASPT2 + PM-CASSCF)

XUV ONLY – TRAJECTORIES



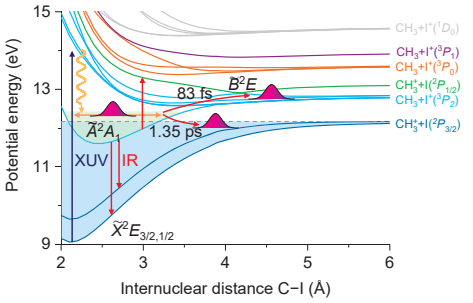
Trajectories show that the wave packet mainly remains in the $\tilde{A}\,^2A_1$ state oscillating (blue lines), while a minor fraction has enough energy to dissociate into CH_3 + I^+ (red lines).

PUMP - DUMP



No dynamics are expected from the $\tilde{X}\,^2E_{3/2,\,1/2}$ states. Dynamics come from the $\tilde{A}\,^2A_1$ state: a pump mechanism where the IR promotes the wave packet to the $\tilde{B}$ states producing I^+ with low KER or a dump mechanism to the $\tilde{X}\,^2E_{3/2,\,1/2}$ states.

PROPOSED MECHANISM



- τ_r=1.3 ps = internal conversion from $\tilde{A}\,^2A_1$ to $\tilde{X}\,^2E_{3/2,\,1/2}$ states induced by the XUV pulse. Less favorable when the IR pulse is launched: Signal depletion in CH_3^+ and enhanced signal of I^+.
- ~83 fs fast decay: competing adiabatic dissociation on the $\tilde{A}\,^2A_1$ state by XUV pulse, reducing the population available for the IR pump process.
- IR probes the oscillating WP in the $\tilde{A}\,^2A_1$ state.
- Short pump-probe delays: No dephase and later revival of the wavepacket.

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